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COMPOUNDED LUBRICANT

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This invention pertains to lubricants having a high degree of oiliness and to compositions for imparting oiliness and film strength to lubricating oils. The invention also pertains to the method of preparing additive materials that impart oiliness and high film strength to lubricants, to blending such additives with lubricating oils and to preparing compounds which have been found to be suitable for use as synthetic lubricants.

In the lubricant art, considerable progress has been realized in recent years in the production of lubricants characterized by one or more specific properties and adapted for particular uses. In the main, this progress can be attributed to two developments: the first, new refining procedures, and the second, addition agents capable of imparting particular properties to available lubricants. Thus, viscosity index improvers and pour depressants are added to automotive lubricants to render the lubricants more adaptable to wide changes in temperature conditions, while other agents are added to improve the load carrying properties of a lubricant which is to be employed, for example, under extreme pressure conditions.

Certain machine elements, such as the hypoid gears commercially used in automotive vehicles, may be subjected at times to extremely heavy pressures of the order of hundreds of thousands of pounds per square inch. Under these conditions, if the film of lubricating oil separating the opposed elements fails, as it is likely to do under such pressure, the surfaces contact each other directly with resultant seizure or excessive wear and early failure. To combat this deficiency in lubricating oils, a group of compounds known as extreme pressure lubricants has been developed. Extreme pressure additives contain active sulfur, phosphorus, chlorine or the like which react with the metal surfaces at the high temperatures generated by friction when machine elements operate at extremely high pressures. The presence of reactive chlorine and the like in a lubricating oil is detrimental in that it subjects the metallic elements lubricated to corrosive action. There is, accordingly, no advantage but, on the contrary, severe disadvantage to using extreme pressure lubricants where they are not absolutely essential.

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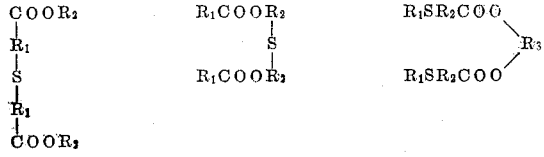
A wide intermediate area lies between lubrication requirements necessitating an extreme pressure lubricant and requirements that may be met satisfactorily with straight run mineral oils. In this area an oil is required having a high film strength but which does not require extreme pressure action.

The new additives of the present invention have been found to have properties which meet the requirements of the intermediate area referred to. These compounds are esters which are characterized by possessing at least two esterified carboxylic groups and at least one sulfur atom in a thioether linkage, by which is meant a group of the type —C—S—C— where the two carbon atoms are components of hydrocarbon groups. More exactly, this preferred class of esters may be described as those possessing at least two groups of the type RCOOR′, where R and R′ are each aliphatic hydrocarbon groups, whether or not connected with other atoms or groups in the molecule. The sulfur atom or atoms which are necessary components of the esters may be present either in the acid or alcohol portion of the molecule. It is preferable that the esters be derived from acids containing 2 to 20 carbon atoms, inclusive of the carbon atoms in the carboxyl group, when the acid is monobasic, or from acids containing 2 to 18 carbon atoms when the acid is dibasic. If monohydric alcohols are employed in the preparation of the esters, those containing 1 to 20 carbon atoms per molecule are suitable, while glycols containing from 2 to 20 carbon atoms per molecule may be employed. Acids, alcohols, and glycols containing oxygen or sulfur in ether or thioether linkages may be employed, and in order to introduce the required atom or atoms of sulfur, at least one such compound must be used. If such atoms of oxygen or sulfur are present, there should be at least one carbon atom between such oxygen or sulfur atom and the carboxyl group or groups in the case of acids and at least two carbon atoms between the oxygen or sulfur atom and the hydroxyl group or groups in the case of alcohols or glycols. The components of the esters should be chosen to provide a ratio between the number of carbon atoms and the number of sulfur atoms which is not greater than 25:1.

A high ratio of sulfur relative to the number

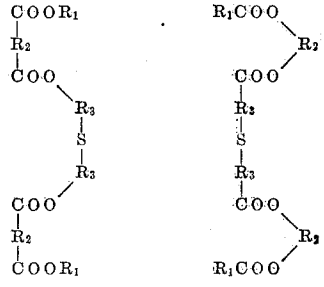
of carbon atoms in the molecule is very desirable in an oiliness agent, since the sulfur is the active component. It will be found that esters of the type defined above provide this high proportion of sulfur. Furthermore, since it is desirable that the additive have low volatility, a compound possessing two ester groups is more desirable than one containing only one ester group because of the lower volatility of the former. It has also been observed that, for the same length of carbon chain, two ester groups provide a greater amount of oiliness characteristics than a single ester group . The compounds herein defined as additives for mineral lubricating oils are therefore unusually desirable for use as oiliness agents.

Several types of esters falling within the above general definition are possible and may be employed for the purpose stated. If the compound contains two ester groups, the following types are those more commonly employed:



In the above formulas R_1, R_2, and R_3 represent aliphatic hydrocarbon groups or chains of aliphatic hydrocarbon radicals interlinked by sulfur atoms.

Esters of a more complex type may also be used. These may be illustrated by the following type formulas, in which R_1, R_2, etc. have the same meaning as before:



The above formulas are illustrative only, and it will be seen that many other types are possible within the general definition given above. Methods of preparing complex esters of the above and other similar types are described in the Smith applications, Serial Nos. 52,428, now Patent No. 2,575,195, 52,429 and 52,430, now Patent No. 2,575,196, all filed October 1, 1948.

As specifically shown in the copending application Serial No. 52,430 mentioned above, of which one of the present inventors is the applicant, the above ester may be prepared by the following general esterification method: In a 1-liter round bottom reaction flask, fitted with a reflux condenser and water trap, there were placed one mol of monobasic acid, one mol of glycol, 2.5 grams of p-toluenesulfonic acid monohydrate (catalyst) and one ml. toluene. The mixture is refluxed until no more water is collected in the water trap. After cooling, 0.5 mol of dibasic acid is added and the refluxing process is resumed until again no more water is collected in the trap. The mixture is washed with three 100 mol. portions of saturated aqueous sodium carbonate solution and one 100 mol. portion of water. After drying with anhydrous calcium sulfonate (such as that sold under the trade name of "Drierite") the material is filtered and stripped at a pressure of about five mm. mercury to a bath temperature of about 225° C.

In preparing the esters of the preferred type, the various components, whether acids, alcohols, or glycols, may be straight chain or branched and either saturated or unsaturated. Typical examples of suitable alcohols include:

Methyl alcohol
Ethyl alcohol
n-Butyl alcohol
Isobutyl alcohol
n-Octyl alcohol
2-ethylhexyl alcohol
Cetyl alcohol
Oleyl alcohol
Ethylene glycol mono-n-butyl ether
Ethylene glycol mono-2-ethylhexyl ether
β-n-Butylmercaptoethanol
β-tert.-Octylmercaptoethanol
Diethylene glycol mono-n-butyl ether
n-Butylmercaptoethoxyethanol
Propylene glycol mono-n-butyl ether

and the like. Many of the above listed and similar ether-alcohols, formed by the reaction of ethylene oxide or propylene oxide with aliphatic alcohols, are known in the industry as "Dowanols," "Carbitols," or "Cellosolves."

Another group of alcohols which is of interest commercially and may be employed when preparing the esters of the present invention are the so-called "Oxo" alcohols, prepared by the reaction of carbon monoxide and hydrogen upon olefins obtainable from petroleum products and hydrogenation of the resulting aldehydes. Materials such as diisobutylene and C_7 olefins are suitable for this purpose, also higher molecular weight olefinic materials are sometimes employed. The alcohols obtained in this manner are primary alcohols and normally have a branched chain structure.

Glycols which may be employed in preparing the preferred esters include butylene glycols, pinacone, trimethylene glycol, tetramethylene glycol, pentamethylene glycol, and the like. Since the glycols may also contain oxygen or sulfur atoms, compounds such as diethylene glycol, triethylene glycol, thiodiglycol, and homologs thereof may likewise be employed. There may also be used glycols containing both oxygen and sulfur, such as bis-[2-(2-hydroxy-ethoxy) ethyl] sulfide.

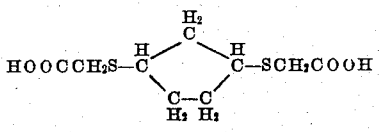
Illustrative examples of monobasic acids which may be employed in the preparation of esters of this invention include acetic acid, valeric acid, butyric acid, caprylic acid, lauric acid, stearic acid, undecylenic acid, oleic acid, β-methoxypropionic acid, β-ethylmercaptopropionic acid, β-tert.-octylmercaptopropionic acid, thioglycolic acid, and the like.

Illustrative examples of dibasic acids which may be employed are the following:

Oxalic acid
Malonic acid
Succinic acid
Adipic acid
Sebacic acid
C_4–C_{24} Alkenyl succinic acid
Diglycolic acid
Thiodiglycolic acid
Thiodipropionic acid
4,10-di-oxa-7-thia-1,13-tridecanedioic acid

In addition to the above, it has been found

advantageous to prepare esters from dibasic acids which are addition products of unsaturated dibasic acids and alcohols or mercaptans or of monobasic hydroxy and/or mercapto aliphatic acids and diolefins. For example, two mols of thioglycolic acid and one mol of cyclopentadiene may be reacted together to form a product probably having a composition of the type



and such an acid may be reacted with alcohols to form esters suitable for use in accordance with the present invention. Similarly, thioglycolic acid may be reacted with isoprene or other diolefins. In a similar manner addition products may be formed between unsaturated acids, e. g., maleic acid, and alcohols or mercaptans. The addition product of a maleic acid ester and dodecyl mercaptan is an example of such a product. Such addition products may be conveniently formed by bubbling air through a mixture of the mercapto acid and olefin or by refluxing the unsaturated ester with the mercaptan in the presence of an acid catalyst such as $SnCl_4$. Another type of adduct may be formed by reacting together two mols of oleic acid, two mols of tert.-octylmercaptan, and one mol of sulfur dichloride. In this case it is believed that the two oleic acid molecules are joined by a sulfur atom and that the tert.-octylmercapto groups become attached to the carbon atoms adjacent to the sulfur linked carbon atoms to form an alkyl mercapto-substituted dibasic acid containing a thioether linkage.

The esters employed in accordance with the present invention may be prepared by the usual esterification methods, in which esterification catalysts such as p-toluenesulfonic acid may be advantageously employed.

In the following table will be shown Almen machine data obtained in submitting mineral oil solutions containing 6% by weight of various esters to the Almen machine test under gradual loading conditions. The base oil employed was a conventionally refined Coastal naphthenic oil of 40 seconds viscosity (Saybolt) at 210° F. The unblended mineral oil carried not more than two weights on the Almen machine. The esters employed will be designated by the components, such as acid, alcohol and/or glycol, or mixtures of these, employed in forming the ester.

Acid	Alcohol or Glycol	Almen Machine Weights Carried
Ethylmercaptoacetic	Polypropylene glycol*	7
β-tert.-Octylmercaptopropionic	Hexamethylene glycol	5
Do	Triethylene glycol	9
Do	Tetraethylene glycol	11
Thiodipropionic	C_9 "Oxo" alcohol	8
Do	Butyl Carbitol	9
4,7-Di-thia-1, 10-decane-dioic	do	13
Adduct: 1 mol Thioglycolic, 1 mol Undecylenic	Isoamyl alcohol	14
Adduct: 1 mol Thioglycolic, 1 mol Undecylenic	Butyl Cellosolve	15
Adduct: 1 mol Thioglycolic, 1 mol Isoprene	n-Decyl alcohol	5
Adduct: 2 mols Thioglycolic, 1 mol Isoprene	do	5
Adduct: 2 mols Thioglycolic, 1 mol Cyclopentadiene	do	15
Adduct: 2 mols Oleic, 1 mol Sulfur dichloride, 2 mols tert.-Octylmercaptan	n-Dodecyl alcohol	7
Adduct: 2 mols Oleic, 1 mol Sulfur dichloride, 2 mols tert.-Octylmercaptan	Isopropyl alcohol	9
Caprylic	Thiodiglycol	11
2 mols Adipic	2 mols n-Butyl, 1 mol Thiodiglycol	9
Do	2 mols Ethyl Cellosolve, 1 mol Thiodiglycol	6
2 mols Thiodipropionic	2 mols n-Butyl, 1 mol Trimethylene glycol	9
2 mols Butyric, 1 mol Thiodipropionic	2 mols Thiodiglycol	15

*Molecular weight equals 400.

From the foregoing data it will be seen that esters of the type herein defined as the preferred additives are efficient in enhancing the load carrying capacity of mineral lubricating oil. It will be understood, of course, that compositions of the type referred to above may be added in various quantities to various types of oils, as will be obvious to those skilled in the art. They may be added to spindle oils, turbine oils, machine oils, cutting oils, and in general to any types of lubricating oils for the purpose of imparting oiliness or mild extreme pressure properties to the same. They may also be used in soluble cutting oils in conjunction with sodium sulfonates or other appropriate emulsifying agents. For the uses stated, proportions of 2 to 10% by weight of the additives are preferred; however, proportions as low as 1% and as high as 20% may occasionally be employed. For concentrates, to be added to oils by the consumer according to his needs, the additive products of this invention may be marketed straight or in 10 to 80% solutions in mineral oil of appropriate grade.

Various conventional additives may be employed in connection with the extreme pressure compound described above, such as thickeners,

oiliness agents, oxidation inhibitors, tackiness agents, viscosity index improvers, pour point depressants, and the like. These materials may also be used in greases thickened with soaps, carbon blacks, silica gels and other known grease-forming materials.

What is claimed is:

1. A mineral lubricating oil containing dissolved therein 1 to 20% by weight of an ester of the formula

$$R_1—COO—R_2—OOC—R_3—S—R_3—COO—R_2—OOC—R_1$$

where R_1 is an aliphatic hydrocarbon radical containing 1 to 18 carbon atoms, R_2 is a radical containing 2 to 8 carbon atoms and is a member of the group consisting of aliphatic hydrocarbon radicals and chains of aliphatic hydrocarbon radicals interlinked by sulfur atoms, and R_3 is an aliphatic hydrocarbon radical containing not more than 8 carbon atoms, wherein the ratio of carbon to sulfur atoms does not exceed 25:1.

2. A mineral lubricating oil containing dissolved therein 1 to 20% by weight of a complex ester of the type defined in claim 1 and prepared from two molecular proportions of butyric acid, one molecular proportion of thiodipropionic acid, and two molecular proportions of thiodiglycol.

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